

Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 8.¹ Synthesis of the Trimetal Compounds $[M\{W(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}_2]$ (M = Ni, Pd, or Pt) and Crystal Structures of the Platinum and Nickel Complexes

By T. V. Ashworth, Michael J. Chetcuti, Judith A. K. Howard, F. Gordon A. Stone, Simon J. Wisbey, and Peter Woodward, Department of Inorganic Chemistry, The University, Bristol BS8 1TS

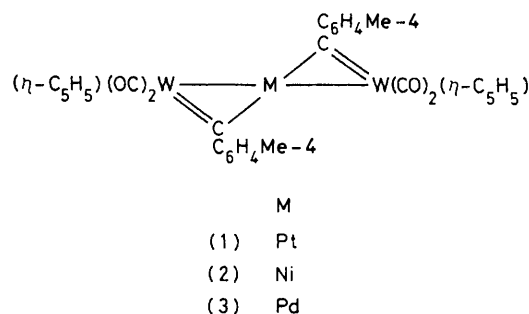
The alkylidyne complex $[W(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ reacts in 1 : 2 mol ratio with the compounds $[\text{Pt}(\text{C}_2\text{H}_4)_3]$, $[\text{Pd}(\text{C}_7\text{H}_{10})_3]$, and $[\text{Ni}(\text{cod})_2]$ (cod = cyclo-octa-1,5-diene) to give the trimetalla species $[M\{W(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}_2]$ (M = Pt, Pd, or Ni), characterised spectroscopically. Additionally, the structures of the platinum and nickel compounds have been established by single-crystal X-ray diffraction studies. Crystals of the platinum compound are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 12.187(6)$, $b = 13.404(7)$, $c = 16.938(9)$ Å, and $\beta = 96.42(4)^\circ$. The structure has been solved by heavy-atom methods and refined by least squares to R 0.047 (R' 0.048) for 4 369 independent diffracted intensities measured at 200 K. For the nickel compound the crystals are monoclinic, space group $P2_1/n$, with $Z = 4$, in a unit cell of dimensions $a = 7.980(2)$, $b = 22.080(6)$, $c = 16.025(3)$ Å, and $\beta = 103.45(2)^\circ$. Intensities were measured at room temperature to $2\theta = 65^\circ$ and the structure has been refined to R 0.053 (R' 0.063) for 5 246 unique reflections. The two molecules have similar structures with a metal atom sequence W–Pt(Ni)–W in which the Pt–W or Ni–W bonds are bridged by alkylidyne ligands, $\text{CC}_6\text{H}_4\text{Me-4}$, affording two three-membered orthogonal ring systems sharing a common vertex (Pt or Ni). In the nickel compound the W–Ni–W sequence is nearly linear (175°), whereas in the platinum complex the angle W–Pt–W is 165° . The W– μ -C bond lengths in both compounds are very similar [1.91(1) and 1.89(1) Å], and suggest a bond order of *ca.* 2 between the tungsten atom and the bridging carbon atom. The metal–metal distances [mean Ni–W 2.584(1), mean Pt–W 2.713(1) Å] also imply multiple bonding within the dimetallacyclopropene rings. Each tungsten atom carries two carbonyl groups, one of which is semi-bridging to the Pt(Ni) atom and lies in the plane of the corresponding cyclopropene ring, while the other is orthogonal to this plane. The dihedral angle between the two dimetallacyclopropene rings is *ca.* 97° . A fascinating difference between these two molecules is that, whereas in the nickel compound the terminal carbonyl groups on the tungsten atoms each lie *trans* to the tolyl group of the second metallacyclopropene ring, in the platinum compound the corresponding carbonyl ligands lie one *cis* and one *trans*.

We have previously drawn an analogy between the interaction of low-valent metal complexes with alkynes, and the reactions of these same compounds with alkylidyne–metal systems which afford complexes containing dimetallacyclopropene rings.^{2,3} In this paper we demonstrate further similarity in chemical behaviour between alkynes and mononuclear metal-carbyne compounds. It is known that tris(ethylene)platinum reacts with alkynes to afford bis(alkyne)platinum complexes $[\text{Pt}(\text{RC}_2\text{R})_2]$.⁴ The possibility thus arises as to whether compounds of formulation $[\text{Pt}(\text{RCML}_n)_2]$ (ML_n = metal–ligand system) are capable of existence. We have, therefore, studied the reaction between $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ ⁵ and the tungsten-carbyne compound $[W(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$,⁶ in 1 : 2 mol ratio, with the objective of preparing a trimetallic species containing a $\text{W}(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{Pt}(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{W}$ atom framework.

RESULTS AND DISCUSSION

Reaction of one equivalent of $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ with two equivalents of $[W(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ in pentane at -40°C , followed by warming to ambient temperatures, affords in over 70% yield a dark purple compound formulated as the trimetal species (1) on the basis of microanalysis and spectroscopic properties. The ^1H n.m.r. spectrum (see Experimental section) showed signals corresponding to those expected for the protons present. The ^{13}C - $\{^1\text{H}\}$ n.m.r. spectrum showed a resonance at δ (p.p.m.) 307, with $J(\text{PtC})$ 830 and $J(\text{WC})$ 157

Hz. This chemical shift is characteristic of an alkylidyne-carbon atom signal, and may be compared with those observed at 300 and 336 p.p.m. in the spectra of the compounds $[W(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ⁶ and $[\text{PtW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PMe}_2\text{Ph})_2(\eta\text{-C}_5\text{H}_5)]$,² respectively. The appearance of the ^{195}Pt and ^{183}W satellites on the alkylidyne-carbon resonance in the ^{13}C n.m.r.



spectrum of (1) is in agreement with the skeletal $\text{W}(\mu\text{-CR})\text{Pt}(\mu\text{-CR})\text{W}$ structure shown. The ^{13}C n.m.r. spectrum also had peaks corresponding to the other carbon nuclei present, including resonances for CO ligands at δ 226 [$J(\text{WC})$ 178] and 221 p.p.m. [$J(\text{WC})$ 178 Hz]. The ^{195}Pt n.m.r. spectrum of (1) showed a resonance at 1 651 p.p.m. [$J(\text{WPt})$ 177 Hz].

The i.r. spectrum (in cyclohexane) of (1) showed carbonyl stretching bands at 1 965, 1 942, and 1 828 cm^{-1} . The latter is too low for a normal terminal

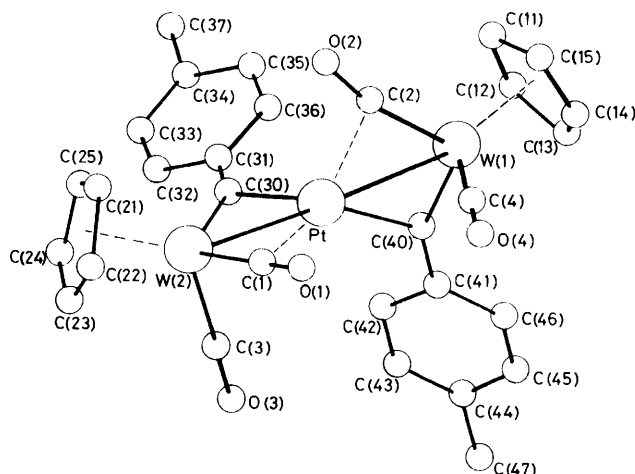


FIGURE 1 Molecular structure of the complex $[\text{PtW}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (1), showing the crystallographic numbering

carbonyl group. A similar low-frequency band (1818 cm^{-1}) is also observed in the spectrum of the dimetal compound $[\text{PtW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PMe}_2\text{Ph})_2(\eta\text{-C}_5\text{H}_5)]$. However, an X-ray diffraction study² of the latter revealed the absence of semi-bridging CO ligands of the classical type,⁷ since the W-C-O angles are $174.6(8)$ and $171.7(8)^\circ$. However, these values, together with the

TABLE 1

Atomic positional (fractional co-ordinates) parameters for the complex $[\text{PtW}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (1), with estimated standard deviations in parentheses

Atom	x	y	z
Pt	0.280 32(4)	0.460 85(4)	0.259 52(3)
W(1)	0.092 58(4)	0.379 41(4)	0.184 98(3)
W(2)	0.477 04(4)	0.553 73(4)	0.295 97(3)
C(1)	0.452 2(12)	0.454 4(11)	0.210 1(8)
O(1)	0.461 8(8)	0.393 5(8)	0.160 7(6)
C(2)	0.159 4(11)	0.503 7(10)	0.149 7(7)
O(2)	0.184 3(9)	0.575 0(8)	0.115 7(6)
C(3)	0.421 9(11)	0.661 0(10)	0.221 4(7)
O(3)	0.389 3(9)	0.725 5(9)	0.180 1(7)
C(4)	0.004 1(13)	0.465 9(10)	0.252 4(10)
O(4)	-0.045 1(10)	0.512 2(9)	0.291 6(7)
C(30)	0.343 5(10)	0.556 3(9)	0.345 0(7)
C(31)	0.280 8(10)	0.587 7(10)	0.408 8(7)
C(32)	0.305 4(10)	0.679 2(10)	0.445 8(7)
C(33)	0.249 3(11)	0.710 3(10)	0.509 5(7)
C(34)	0.169 6(11)	0.652 1(11)	0.536 0(7)
C(35)	0.146 3(10)	0.561 1(11)	0.500 3(8)
C(36)	0.199 8(10)	0.527 3(10)	0.437 4(7)
C(37)	0.109 1(13)	0.687 7(13)	0.603 4(9)
C(40)	0.195 0(11)	0.334 4(9)	0.270 9(8)
C(41)	0.231 5(11)	0.257 9(9)	0.328 8(7)
C(42)	0.160 1(10)	0.182 3(10)	0.345 1(7)
C(43)	0.192 7(12)	0.102 1(12)	0.391 9(8)
C(44)	0.301 4(13)	0.092 1(11)	0.426 5(8)
C(45)	0.372 7(12)	0.170 1(11)	0.415 0(8)
C(46)	0.341 3(11)	0.251 2(10)	0.365 9(9)
C(47)	0.341 8(14)	0.001 7(12)	0.476 0(9)
C(11)	-0.073 7(12)	0.324 9(12)	0.113 4(12)
C(12)	-0.003 4(18)	0.349 2(12)	0.057 6(10)
C(13)	0.090 1(14)	0.285 7(11)	0.067 0(9)
C(14)	0.075 8(11)	0.219 3(10)	0.129 8(8)
C(15)	-0.027 1(11)	0.242 6(11)	0.156 9(9)
C(21)	0.629 6(12)	0.649 9(11)	0.338 3(10)
C(22)	0.669 5(11)	0.571 0(13)	0.300 8(8)
C(23)	0.647 3(12)	0.481 5(12)	0.342 2(10)
C(24)	0.599 5(12)	0.509 8(15)	0.407 8(9)
C(25)	0.587 7(13)	0.619 7(18)	0.405 6(10)

TABLE 2

Internuclear distances (\AA) and angles ($^\circ$) for $[\text{PtW}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (1), with estimated standard deviations in parentheses

(a) Distances

Pt-W(1)	2.715(1)	Pt-W(2)	2.711(1)
W(1)-C(2)	1.98(1)	C(2)-O(2)	1.17(2)
W(1)-C(4)	2.02(2)	C(4)-O(4)	1.13(2)
W(2)-C(1)	1.97(1)	C(1)-O(1)	1.19(2)
W(2)-C(3)	1.98(1)	C(3)-O(3)	1.15(2)
W(2)-C(30)	1.91(1)	W(1)-C(40)	1.91(1)
Pt-C(30)	2.02(1)	Pt-C(40)	2.01(1)
Pt-C(1)	2.34(2)	Pt-C(2)	2.31(1)
C(30)-C(31)	1.45(2)	C(40)-C(41)	1.45(2)
Mean C-C(tolyl) = 1.39(1)			
C(34)-C(37)	1.51(2)	C(44)-C(47)	1.52(2)
W(1)-C(11)	2.34(2)	W(2)-C(21)	2.31(1)
W(1)-C(12)	2.37(2)	W(2)-C(22)	2.35(1)
W(1)-C(13)	2.36(1)	W(2)-C(23)	2.34(2)
W(1)-C(14)	2.34(1)	W(2)-C(24)	2.35(2)
W(1)-C(15)	2.36(1)	W(2)-C(25)	2.34(2)
C(11)-C(12)	1.38(3) *	C(12)-C(13)	1.42(3)
C(13)-C(14)	1.41(2)	C(14)-C(15)	1.42(2)
C(15)-C(11)	1.41(2)		

(b) Angles

Pt-W(1)-C(4)	88.9(4)	Pt-W(2)-C(3)	87.7(4)
Pt-W(1)-C(2)	56.5(3)	Pt-W(2)-C(1)	57.5(4)
C(2)-W(1)-C(4)	87.2(6)	C(1)-W(2)-C(3)	90.4(5)
Pt-W(1)-C(40)	47.7(4)	Pt-W(2)-C(30)	48.1(4)
C(4)-W(1)-C(40)	95.5(6)	C(1)-W(2)-C(30)	105.4(6)
C(2)-W(1)-C(40)	104.0(5)	C(3)-W(2)-C(30)	91.1(5)
W(1)-Pt-W(2)	165.5(0)		
W(1)-Pt-C(2)	45.4(3)	W(2)-Pt-C(1)	45.2(3)
W(1)-Pt-C(1)	124.0(3)	W(2)-Pt-C(2)	122.5(3)
C(1)-Pt-C(2)	103.7(5)	C(30)-Pt-C(40)	128.8(5)
W(1)-Pt-C(40)	44.5(4)	W(2)-Pt-C(30)	44.7(4)
W(1)-Pt-C(30)	145.3(4)	W(2)-Pt-C(40)	145.1(4)
C(2)-Pt-C(40)	90(1)	C(1)-Pt-C(30)	90(1)
C(2)-Pt-C(30)	125.2(5)	C(1)-Pt-C(40)	119.8(5)
W(1)-C(2)-O(2)	167(1)	W(2)-C(1)-O(1)	166(1)
W(1)-C(4)-O(4)	178(1)	W(2)-C(3)-O(3)	178(1)
Pt-C(1)-O(1)	116(1)	Pt-C(2)-O(2)	115(1)
W(1)-C(2)-Pt	78.1(4)	W(2)-C(1)-Pt	77.4(5)
W(1)-C(40)-Pt	87.8(5)	W(2)-C(30)-Pt	87.3(5)
W(1)-C(40)-C(41)	150(1)	W(2)-C(30)-C(31)	151(1)
Pt-C(40)-C(41)	122(1)	Pt-C(30)-C(31)	122(1)
C(40)-C(41)-C(42)	120(1)	C(30)-C(31)-C(32)	119(1)
C(40)-C(41)-C(46)	123(1)	C(30)-C(31)-C(36)	123(1)
C(43)-C(44)-C(47)	123(1)	C(33)-C(34)-C(37)	120(1)
C(45)-C(44)-C(47)	121(1)	C(35)-C(34)-C(37)	121(1)
C(11)-C(12)-C(13)	110(1)	C(12)-C(13)-C(14)	107(2)
C(13)-C(14)-C(15)	107(1)	C(14)-C(15)-C(11)	109(1)
C(15)-C(11)-C(12)	107(1)		

* Atoms in C(21)-(25) ring less well defined, C-C(mean) = 1.40(2) \AA .

small Pt-W-CO angles of 72.0 and 67.4° suggest a di-metal carbonyl interaction of the type invoked⁸ for $[\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]_2$ [ν_{CO} 1859 cm^{-1} , average angle Mo-C-O 176° , average Mo-Mo-CO 67.4°]⁸ and $[\text{V}_2(\text{CO})_5(\eta\text{-C}_5\text{H}_5)_2]$ [ν_{CO} 1826 cm^{-1} (ref. 9), average bridging V-C-O 169° (ref. 10)]. Thus, in view of the i.r. evidence for a bridging carbonyl interaction of some kind in (1), as well as the considerable novelty of the proposed structure as a whole, a single-crystal X-ray diffraction study was carried out.

The X-ray diffraction results for (1) are summarised in Tables 1-3, and the molecular structure is shown in Figure 1, together with the atom-numbering scheme. The data confirm that the molecule contains a W-Pt-W framework with the two Pt-W bonds bridged by CC_6H_4 -

TABLE 3

Some least-squares planes * for the complex (1); distances (Å) of atoms from the planes are given in square brackets

(i): Pt, W(1), C(40)
 $7.430x - 5.994y - 12.169z = -3.838$

(ii): Pt, W(2), C(30)
 $3.202x - 10.385y + 9.177z = -1.506$

(iii): C(40), C(41)—(46), C(47)
 $-4.268x + 6.703y + 13.993z = 5.304$
 [C(40) -0.12; maximum deviation in ring 0.05]

(iv): C(30), C(31)—(36), C(37)
 $7.695x - 5.857y + 9.585z = 2.653$

[C(30) 0.04; maximum deviation in ring 0.05]

(v): Pt, W(1), C(2)
 $7.460x - 7.125y - 11.010z = -4.049$

(vi): Pt, W(2), C(1)
 $2.684x - 9.792y + 10.458z = -1.046$

Angles (°) between the least-squares planes:

(i)-(ii)	97	(i)-(iii)	17
(iv)-(ii)	29	(i)-(v)	6
(vi)-(ii)	5	(vi)-(v)	98

* *x*, *y*, and *z*, are fractional crystal co-ordinates.

Me-4 groups. The trimetallic sequence however is not linear [W(1)-Pt-W(2) 165.5°]. The Pt-W separations [mean 2.713(1) Å] are shorter than those found [2.830(2) Å] in the *triangulo*-diplatinumtungsten complex [Pt₂W{μ-C(OMe)Ph}(CO)₆(PBu^tMe)₂]¹¹ but are close to that found [2.751(1) Å] in the bridging alkylidyne complex [PtW(μ-CC₆H₄Me-4)(CO)₂(PMe₂Ph)₂(η-C₅H₅)].² In the alkylidene-bridged dimetal species [PtW{μ-C(OMe)R}(CO)₄(L)(PMe₃)₂] the Pt-W distances are 2.861(1) Å (R = Ph, L = CO)¹² and 2.825(1) Å (R = C₆H₄Me-4, L = PMe₃).¹³ It is thus apparent that an alkylidyne-bridged Pt-W bond is significantly shorter than one bridged by an alkylidene ligand, and this point is discussed further below.

The W-μ-C distances in (1) [mean 1.907(13) Å] compare with 1.967(6) Å found² for the corresponding bond length in [PtW(μ-CC₆H₄Me-4)(CO)₂(PMe₂Ph)₂(η-C₅H₅)], and both these distances are notably longer than the carbon-tungsten distance [1.82(2) Å] in [W(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)].⁶ It is interesting to compare the W-μ-C distance in (1) with that found [2.14(2) Å] for the tungsten-carbene carbon bond length in [W(=CPh₂)(CO)₅].¹⁴ It appears that the W-μ-C separations in (1) correspond approximately to that expected for a carbon-tungsten double bond, carbon-tungsten single bonds being considerably longer.¹³ Moreover, in the formation of (1) from [W(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)] the observed increase in W-C distance (*ca.* 0.1 Å) parallels the increase in C-C distance observed on bonding an alkyne to Pt⁹ in a complex.¹⁵ The mean Pt-μ-C distance [2.015(10) Å] in (1) is very similar to that previously found [1.997(9) Å] in [PtW(μ-CC₆H₄Me-4)(CO)₂(PMe₂Ph)₂(η-C₅H₅)],² and is at the lower end of the range (1.99—2.15 Å) generally measured for carbon-platinum σ bonds.¹⁶

The bridging CC₆H₄Me-4 ligands in (1) define planes

inclined at 17 and 29°, respectively, to the planes defined by the two dimetallacyclopentene rings. This is in marked contrast to the situation occurring in [PtW(μ-CC₆H₄Me-4)(CO)₂(PMe₂Ph)₂(η-C₅H₅)]² where the corresponding dihedral angle is much larger at 88°. As indicated by the i.r. spectrum, complex (1) has two semi-bridging carbonyl groups [W(1)-C(2)-O(2) 167(1)°, and W(2)-C(1)-O(1) 166(1)°] but these are of the well established type.⁷ In accord with the bending at C(1) and C(2), the distances Pt-C(1) and Pt-C(2) [mean 2.33(1) Å] come near to the longer of the asymmetric Pt-μ-CO distances [2.21(3) Å] in the *triangulo*-triplatinum complex [Pt₃(μ-CO)₃{P(C₆H₁₁)₃}]¹⁷. If in (1) the atoms C(1) and C(2) were fully σ bonded to the platinum the metal would have a 16-electron configuration, rather than 14 in the absence of such bonds. However, electron counts for the metal atoms in a structure of this type neglect the probability of electron delocalisation in the two dimetallacyclopentene rings which join at the platinum. The dihedral angle between the planes defined by these two rings is 97° (Table 3), and it is interesting to compare this value with the angle found (98°) between the two C₂Pt planes in the bis(alkyne)-platinum complex [Pt(PhC₂Ph)₂].⁴ However, in (1) the angles at the platinum atom formed by W(1), W(2), C(20), and C(40) are far from tetrahedral. The constraints of the two dimetallacyclopentene rings lead to W-Pt-μ-C angles of 45° so that the angles W(2)-Pt-C(40) and W(1)-Pt-C(30) are 145°. The two sets of atoms, Pt-W(2)-C(1) and Pt-W(1)-C(2), involving the bridging CO ligands also define planes with a dihedral angle (98°) not far from that expected for a tetrahedral arrangement about the platinum, but again the four atoms C(1), W(2), C(2), and W(1) form non-tetrahedral angles at the metal of 45, 123, 45, and 124°. For each half of the molecule, however, the dimetallacyclopentene ring and the corresponding bridging carbonyl are nearly coplanar (Table 3). The packing of the molecules within the unit cell is shown in Figure 2.

Having fully characterised complex (1), it was of interest to establish whether analogous compounds would be formed by nickel and by palladium. Accordingly, reactions between [W(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)] and [Ni(cod)₂]¹⁸ (cod = cyclo-octa-1,5-diene), and between the tungsten compound and [Pd(dba)₂]¹⁹ (dba = dibenzylideneacetone) were investigated. In this manner complexes (2) and (3) were isolated, respectively. However, it was found difficult to separate (3) from dba released in the reaction from the [Pd(dba)₂], and this led to the discovery that compound (3) was best prepared by treating [W(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)] with tris(bicyclo[2.2.1]heptene)palladium.⁵ Complex (3) is the least stable of the three trimetal species prepared. Its solutions in organic solvents decompose rapidly, in contrast to those of (1) and (2). Moreover, the platinum and nickel compounds (1) and (2) are stable as solids in air for periods of several weeks, whereas (3) decomposes even as a solid in less than a week.

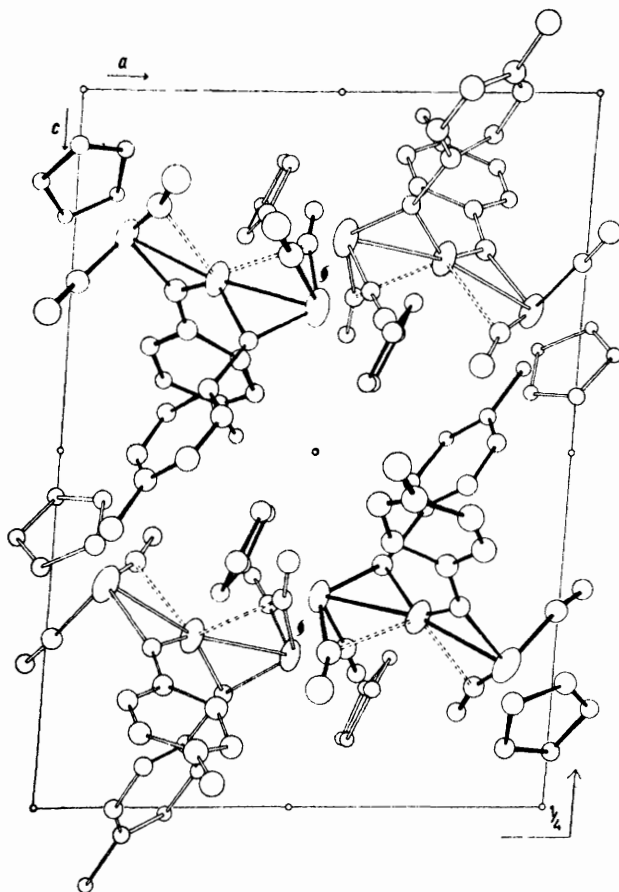


FIGURE 2 Contents of the monoclinic unit cell for complex (1) seen in projection down b looking towards the origin. Some symmetry element symbols have been omitted because of coincidence with atom locations

The spectroscopic properties of (2) and (3) are generally similar to those of (1), and are therefore in accord with the proposed structures. The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra

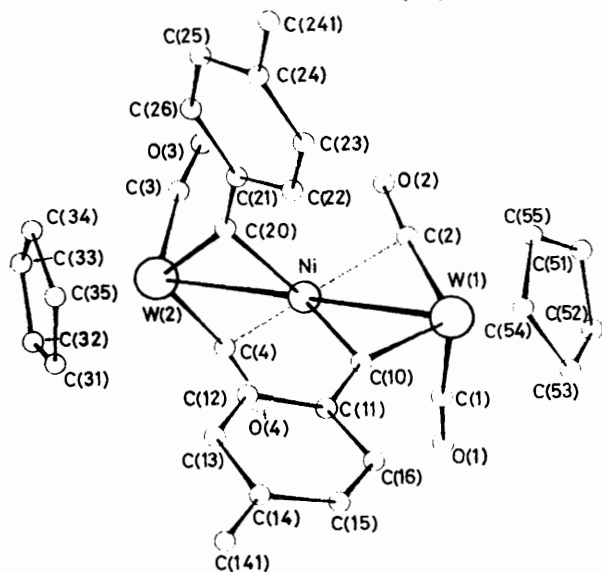


FIGURE 3 Molecular structure of complex $[\text{NiW}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (2), showing the crystallographic numbering

for (2) and (3) show resonances for alkylidyne carbon atoms at δ 315 [$J(\text{WC})$ 171] and 305 p.p.m. [$J(\text{WC})$ 171 Hz], respectively. The ^1H n.m.r. spectra also show the expected signals for the various groups, the peaks having the anticipated relative intensities. The i.r. spectra of (2) and (3), measured in solution, each show three CO absorptions, with one band at relatively low frequency, *viz.* 1 818 cm^{-1} for (2) and 1 805 cm^{-1} for (3). The spectra thus suggest that semi-bridging CO ligands are present in the structures. Indeed, measurement of the i.r. spectrum of (2) in Nujol revealed a band at 1 782 cm^{-1} , raising the possibility that the nickel compound contained a fully bridging carbonyl group. An X-ray diffraction study was therefore carried out to establish its structure, and to relate it to that of (1).

The molecular structure is shown in Figure 3, with the atomic numbering scheme, and the structural data are summarised in Tables 4–6. The structure of (2) is closely similar to that of (1), except in two significant respects: (i) the metal atom axis is more nearly linear

TABLE 4

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for the compound $[\text{NiW}_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (2)

Atom	x	y	z
Ni	0.391 40(5)	0.662 77(5)	0.276 50(6)
W(1)	0.262 30(5)	0.598 84(2)	0.381 10(2)
W(2)	0.529 84(5)	0.734 13(2)	0.183 52(2)
C(1)	0.458(2)	0.627 3(5)	0.474 5(6)
O(1)	0.569(1)	0.641 1(5)	0.529 3(5)
C(2)	0.205(1)	0.682 0(5)	0.347 4(5)
O(2)	0.143(1)	0.732 0(3)	0.333 8(5)
C(3)	0.389(2)	0.802 4(5)	0.209 0(7)
O(3)	0.305(2)	0.842 3(5)	0.220 8(7)
C(4)	0.622(1)	0.717 2(4)	0.305 5(6)
O(4)	0.702(1)	0.709 0(3)	0.376 6(4)
C(10)	0.413(1)	0.580 1(4)	0.308 8(5)
C(11)	0.505(1)	0.535 8(4)	0.268 0(5)
C(12)	0.558(1)	0.547 1(5)	0.192 2(6)
C(13)	0.635(1)	0.502 5(5)	0.153 7(7)
C(14)	0.667(1)	0.445 2(5)	0.190 3(8)
C(15)	0.618(2)	0.435 4(6)	0.263 8(9)
C(16)	0.541(2)	0.479 5(5)	0.304 5(7)
C(141)	0.753(2)	0.397 6(7)	0.148 1(10)
C(20)	0.332(1)	0.684 9(3)	0.159 2(5)
C(21)	0.183(1)	0.658 7(3)	0.098 1(5)
C(22)	0.122(1)	0.599 8(4)	0.106 1(6)
C(23)	-0.014(1)	0.577 8(5)	0.044 9(7)
C(24)	-0.094(1)	0.611 5(5)	-0.026 3(6)
C(25)	-0.034(1)	0.668 7(5)	-0.034 9(6)
C(26)	0.103(1)	0.693 9(4)	0.026 2(5)
C(241)	-0.246(2)	0.586 0(7)	-0.089 5(6)
C(31)*	0.782(2)	0.699(1)	0.140(1)
C(32)	0.803(2)	0.762(1)	0.156(1)
C(33)	0.672(2)	0.793(1)	0.096(1)
C(34)	0.569(2)	0.749(1)	0.043(1)
C(35)	0.637(2)	0.691(1)	0.070(1)
C(41)*	0.585(3)	0.713(1)	0.052(2)
C(42)	0.538(3)	0.775(1)	0.050(2)
C(43)	0.664(3)	0.806(1)	0.113(2)
C(44)	0.790(3)	0.763(1)	0.153(2)
C(45)	0.741(3)	0.706(1)	0.116(2)
C(51)	0.123(2)	0.551(1)	0.478(1)
C(52)	0.002(2)	0.581(1)	0.423(1)
C(53)	-0.012(2)	0.554(1)	0.341(1)
C(54)	0.117(3)	0.508(1)	0.353(1)
C(55)	0.195(2)	0.506(1)	0.438(1)

* C(31)–(35) and C(41)–(45) refer to the disordered C_5H_5 ring (see text).

(175° instead of 165°); (ii) one of the terminal carbonyl ligands points in the opposite direction, giving the central framework of the molecule two-fold rotational symmetry not possessed by the platinum analogue. The separations between the tungsten atoms and the bridging alkylidyne carbon atoms are, within experimental error, the same as those found in (1). The Ni-μ-C distances [1.89(1) Å] may be compared with the Ni-C σ bonded distances in [NiMe(acac){P(C₆H₁₁)₃}] (acac = acetylacetonate) [1.94(1) Å],²⁰ [Ni(acac)(C₈H₁₃)] [1.95(2) Å],²¹ and [Ni(C₆H₅)(PPh₃)(η-C₅H₅)] [1.90(1) Å].²² The nickel-tungsten bond lengths [mean 2.584(1) Å] are considerably shorter than expected (ca. 2.8 Å) based on the sum of a W radius of 1.61 Å {obtained from half the W-W bond length of 3.222(1) Å in [W₂(CO)₆(η-C₅H₅)₂]}²³ and a mean Ni radius of ca. 1.2 Å {deduced from half the

TABLE 5

Internuclear distances (Å) and angles (°) for [NiW₂(μ-CC₆H₄Me-4)₂(CO)₄(η-C₅H₅)₂] (2) with estimated standard deviations in parentheses *

(a) Distances			
Ni-W(1)	2.582(1)	Ni-W(2)	2.586(1)
W(1)-C(1)	2.00(1)	C(1)-O(1)	1.14(1)
W(1)-C(2)	1.94(1)	C(2)-O(2)	1.21(1)
W(2)-C(3)	1.98(1)	C(3)-O(3)	1.15(2)
W(2)-C(4)	1.96(1)	C(4)-O(4)	1.18(1)
W(1)-C(10)	1.902(9)	W(2)-C(20)	1.883(8)
Ni-C(10)	1.895(8)	Ni-C(20)	1.893(7)
Ni-C(2)	2.12(1)	Ni-C(4)	2.15(1)
C(10)-C(11)	1.46(1)	C(20)-C(21)	1.47(1)
Mean C-C(tolyl) = 1.38(1)			
C(14)-C(141)	1.50(2)	C(24)-C(241)	1.49(2)
W(1)-C(51)	2.30(2)	W(1)-C(52)	2.36(2)
W(1)-C(53)	2.35(2)	W(1)-C(54)	2.31(2)
W(1)-C(55)	2.35(2)		
W(2)-C(31) *	2.41(2)	W(2)-C(41) *	2.30(3)
W(2)-C(32)	2.41(2)	W(2)-C(42)	2.33(3)
W(2)-C(33)	2.38(2)	W(2)-C(43)	2.35(3)
W(2)-C(34)	2.36(2)	W(2)-C(44)	2.33(3)
W(2)-C(35)	2.38(2)	W(2)-C(45)	2.30(3)
(b) Angles			
Ni-W(1)-C(1)	87.4(3)	Ni-W(2)-C(3)	90.4(4)
Ni-W(1)-C(2)	53.6(3)	Ni-W(2)-C(4)	54.5(3)
C(1)-W(1)-C(2)	90.3(4)	C(3)-W(2)-C(4)	92.2(4)
Ni-W(1)-C(10)	47.0(2)	Ni-W(2)-C(20)	46.9(2)
C(1)-W(1)-C(10)	91.7(4)	C(3)-W(2)-C(20)	89.6(5)
C(2)-W(1)-C(10)	100.4(4)	C(4)-W(2)-C(20)	101.4(4)
W(1)-Ni-W(2)	174.5(0)		
W(1)-Ni-C(2)	47.5(3)	W(2)-Ni-C(4)	47.7(2)
W(1)-Ni-C(4)	127.9(2)	W(2)-Ni-C(2)	129.4(3)
C(2)-Ni-C(4)	116.4(4)	C(10)-Ni-C(20)	120.4(3)
W(1)-Ni-C(10)	47.3(3)	W(2)-Ni-C(20)	46.6(3)
W(1)-Ni-C(20)	137.7(3)	W(2)-Ni-C(10)	136.0(3)
C(2)-Ni-C(10)	94.5(4)	C(4)-Ni-C(20)	94.3(3)
C(2)-Ni-C(20)	115.8(4)	C(4)-Ni-C(10)	117.3(4)
W(1)-C(1)-O(1)	177(1)	W(2)-C(3)-O(3)	178(1)
W(1)-C(2)-O(2)	167.6(9)	W(2)-C(4)-O(4)	169.7(9)
Ni-C(2)-O(2)	113.2(8)	Ni-C(4)-O(4)	111.4(7)
W(1)-C(2)-Ni	78.9(4)	W(2)-C(4)-Ni	77.8(3)
W(1)-C(10)-Ni	85.7(4)	W(2)-C(20)-Ni	86.4(3)
W(1)-C(10)-C(11)	150.6(7)	W(2)-C(20)-C(21)	150.9(6)
Ni-C(10)-C(11)	123.1(6)	Ni-C(20)-C(21)	122.6(6)
C(10)-C(11)-C(12)	124(1)	C(20)-C(21)-C(22)	123(1)
C(10)-C(11)-C(16)	120(1)	C(20)-C(21)-C(26)	118(1)
C(13)-C(14)-C(141)	120(1)	C(23)-C(24)-C(241)	120(1)
C(15)-C(14)-C(141)	123(1)	C(25)-C(24)-C(241)	122(1)

* Ring C(31)-(35) was found to be positionally disordered with ring C(41)-(45) in the population ratio 0.7 : 0.3. These rings were refined as regular pentagons with fixed C-C distances of 1.395 Å. For C(51)-(55) the mean C-C was 1.38(2) Å.

TABLE 6

Some least-squares planes * for the complex (2); distances (Å) of atoms from the planes are given in square brackets

(i): Ni, W(1), C(10)	$5.033x + 4.938y + 9.231z = 7.795$
(ii): Ni, W(2), C(20)	$4.907x - 16.767y - 5.656z = -10.473$
(iii): C(10), C(11)-(14), C(141)	$6.312x + 7.015y + 5.201z = 8.329$
[C(10) - 0.04; maximum deviation in ring 0.04]	
(iv): C(20), C(21)-(26), C(241)	$6.160x - 8.153y - 10.941z = -5.296$
[C(20) 0.01; maximum deviation in ring 0.02]	
(v): Ni, W(1), C(2)	$4.460x + 7.086y + 9.835z = 9.161$
(vi): Ni, W(2), C(4)	$4.478x - 16.907y - 6.023z = -11.013$

Angles (°) between the least squares planes:

(i)-(ii)	93	(i)-(iii)	17
(iv)-(ii)	30	(i)-(v)	7
(vi)-(ii)	2	(vi)-(v)	96

* *x*, *y*, and *z* are fractional crystal co-ordinates.

observed Ni-Ni distances in K₄[Ni₂(CN)₆],²⁴ and various other dinickel species²⁵. In the anion [Ni₃W₂(CO)₁₆]²⁻ the nickel-tungsten separations average 3.10 Å, but these distances have been taken to reflect the electron deficient nature of these metal-metal bonds,²⁵ and comparison with the nickel-tungsten bond length in (2) is clearly not valid. Even so, it would appear that the metal-metal distances established for (2) are ca. 0.2 Å shorter than expected on the basis of single bonds, and may reflect some multiple-bond character associated with electron delocalisation in the fused dimetallacyclopentene ring systems. A similar contraction (ca. 0.2 Å) of the metal-metal bond is found in (1), based on summing tungsten²³ and platinum²⁶ radii.

As in (1), compound (2) has two semi-bridging CO ligands, the angles W(1)-C(2)-O(2) and W(2)-C(4)-O(4) being 168(1) and 170(1)°, respectively. The Ni-C(2) and Ni-C(4) distances [2.13(1) Å] are, as expected, significantly longer than those recently found [1.83(1) and 1.93(1) Å] for the fully bridging Ni-μ-CO separations in [NiOs₃(μ-H)₂(μ-CO)₂(CO)₈(PPh₃)₂].²⁷

The overall configurations of complexes (1) and (2) are closely similar, even to the extent that the twists of the tolyl rings (Tables 3 and 6) are different for the two portions of the molecule but the same for the two molecules. The unit-cell volumes for the two structures are also closely similar [2 749 (Pt) vs. 2 747 Å³ (Ni)]. In complex (2) there is evidence for some disorder in one of the cyclopentadienyl rings (Table 4). The packing of the molecules in complex (2) is shown in Figure 4, and a stereopair is given in Figure 5. This shows clearly that the CC₆H₄Me-4 ligands bridge the central W-M-W chain on its convex side, and it is presumably the bulkiness of these ligands which causes the dihedral angle between the two W-M-C rings to open up to 98°.

In every case the rotation of the tolyl ring around its C...Me-4 axis is such as to turn the outermost carbon atoms [e.g. C(45) and C(46) in complex (1)] in the same direction as that adopted by the terminal carbonyl group on the adjacent tungsten atom. When viewed along the Me-4...C axis, this means that for the platinum com-

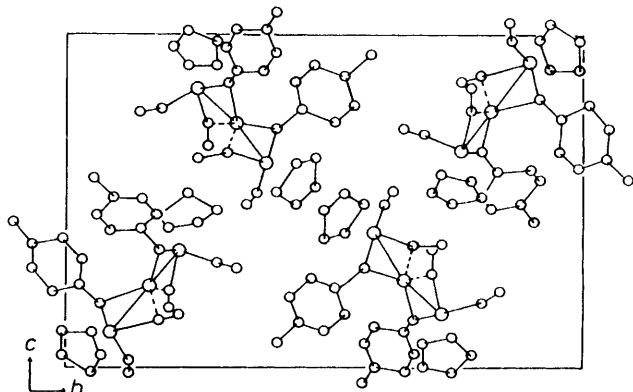


FIGURE 4 Contents of the monoclinic unit cell for complex (2) seen in projection down a^* looking towards the origin

pound one ring rotates clockwise and the other anticlockwise, while for the nickel compound both rings have the same sense of orientation; but as the molecules crystallise in a centrosymmetric space group, the crystals contain equal numbers of enantiomeric molecules. It is not easy to see why the nickel and platinum complexes are not isostructural when their overall molecular geometry is so similar, nor why for both molecules the tolyl twists are the same; this is even more remarkable in view of the fact that the two halves of the molecule are different, seemingly for reasons of crystal packing.

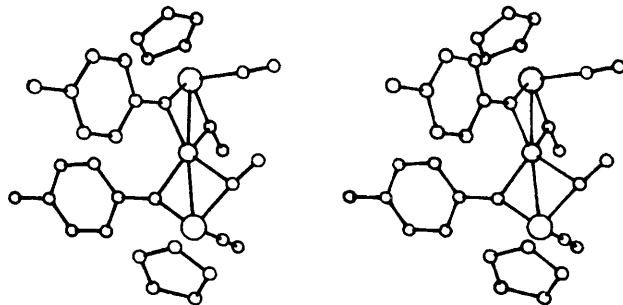


FIGURE 5 Stereoscopic view of the molecular structure of complex (2)

EXPERIMENTAL

Instrumentation used and experimental techniques employed were as described in Part 1.¹² Light petroleum refers to that fraction of b.p. 40–60 °C. Hydrogen-1 and ¹³C-{¹H} n.m.r. spectra were measured at 100 and 25.15 MHz, respectively. For ¹³C spectra chemical shifts δ are in p.p.m. relative to SiMe₄ (positive values to high frequency). Spectra were measured in [²H₁]chloroform (¹H), or [²H₁]chloroform–dichloromethane mixtures (¹³C) at ambient temperatures.

The complexes [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)],⁶ [Pt(C₂H₄)₃],⁵ [Pd(C₇H₁₀)₃],⁵ and [Ni(cod)₂]¹⁸ were prepared as described in the literature.

Synthesis of the Complexes [M{W(CC₆H₄Me-4)(CO)₂(η -C₅H₅)₂}] (M = Ni, Pd, or Pt).—(a) A toluene (30 cm³) solution of [Ni(cod)₂] (0.314 g, 1.14 mmol) was added to a rapidly stirred solution of [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)] (0.93 g, 2.28 mmol) in light petroleum (60 cm³). The mixture turned dark red, and after stirring for 2 h at 25 °C it was chilled (–20 °C) overnight. Solvent was removed *in vacuo* and the residue washed with light petroleum to give red *microcrystals* of [NiW₂(μ -CC₆H₄Me-4)₂(CO)₄(η -C₅H₅)₂] (2) (0.7 g, 70%), m.p. 140–146 °C (decomp.) (Found: C, 40.8; H, 2.9. C₃₀H₂₄NiO₄W₂ requires C, 41.2; H, 2.8%); ν_{\max} (CO) at 1972s, 1952s, 1818m, br (in cyclohexane); ν_{\max} at 1955s, 1924s, 1800m, and 1782s (in Nujol) cm⁻¹. N.m.r.: ¹H, τ 2.70 and 2.96 [(AB)₂ pattern, 8 H, C₆H₄, J (AB) 6 Hz], 4.43 (s, 10 H, C₅H₅), and 7.76 (s, 6 H, Me). ¹³C {[Cr(acac)₃] added}, δ (p.p.m.) 315 [μ -C, J (WC) 171], 231[CO, J (WC) 161], 224 [CO, J (WC) 166], 155 [C(1) (C₆H₄), J (WC) 22 Hz], 138 (CMe), 129, 127 [C(2), C(3) (C₆H₄)], 92 (C₅H₅), and 22 (Me).

(b) Tris(bicyclo[2.2.1]heptene)palladium (2 mmol) was prepared *in situ* at –40 °C in light petroleum and the solution filtered through an alumina pad (10 cm) at –10 °C into a pentane solution of [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)] (1.63 g, 4 mmol) held at –40 °C. The mixture was slowly (4 h) warmed to ambient temperature and stirred (15 h). Solvent was removed *in vacuo* and the black residue extracted with toluene (40 cm³). Chromatography on alumina (75 cm), eluting with toluene, afforded bicyclo[2.2.1]heptene, an orange band of [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)], and finally a slow moving orange-brown band. The solution containing the latter was concentrated to ca. 5 cm³ and pentane added giving black *microcrystals* of [PdW₂(μ -CC₆H₄Me-4)₂(CO)₄(η -C₅H₅)₂] (3) (650 mg, 35%) (Found: C, 39.9; H, 2.4. C₃₀H₂₄O₄PdW₂ requires C, 39.1; H, 2.6%); ν_{\max} (CO) (methyl cyclohexane), 1971s, br, 1853m, and 1805m cm⁻¹. N.m.r.: ¹H, τ 3.1 and 2.5 [(AB)₂ pattern, 8 H, C₆H₄, J (AB) 8 Hz], 4.63 (s, 10 H, C₅H₅), and 7.82 (6 H, Me). ¹³C, δ (p.p.m.) 305 [μ -C, J (WC) 171], 224 [4 CO, J (WC) 180], 153 [C(1) (C₆H₄), J (WC) 24 Hz], 138 (CMe), 129, 128 [C(2), C(3) (C₆H₄)], 91 (C₅H₅), and 22 (Me).

(c) A pentane (10 cm³) solution of [Pt(C₂H₄)₃] (0.6 mmol, generated *in situ*) at –40 °C was treated with a light petroleum (30 cm³) solution of [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)] (1.2 mmol). The mixture was warmed to ambient temperature and rapidly stirred. A red precipitate formed after 10 min, and after 20 min solvent was removed *in vacuo*, and the residue washed with light petroleum (4 × 5 cm³) and dried *in vacuo* affording purple red *crystals* of [PtW₂(μ -CC₆H₄Me-4)₂(CO)₄(η -C₅H₅)₂] (1) (0.5 g, 75%), m.p. 178–180 °C (Found: C, 35.0; H, 2.7. C₃₀H₂₄O₄PtW₂ requires C, 35.6; H, 2.4%); ν_{\max} (CO), 1965m, 1942s, and 1828m, br (cyclohexane); 1953s, 1935s, 1822(sh), 1810(sh), and 1800s (Nujol) cm⁻¹. N.m.r.: ¹H, τ 2.56 and 3.02 [(AB)₂ quartet, 8 H, C₆H₄, J (AB) 8 Hz], 4.36 (s, 10 H, C₅H₅), and 7.80 (s, 6 H, Me); ¹³C {[Cr(acac)₃] added}, δ (p.p.m.) 307 [μ -C, J (PtC) 830, J (WC) 157], 226 [CO, J (WC) 178], 221 [CO, J (WC) 178], 151 [C(1) (C₆H₄), J (PtC) 44], 139 (CMe), 130 [C(2) (C₆H₄), J (PtC) 30 Hz], 129 [C(3) (C₆H₄)], 91 (C₅H₅), and 22 (Me); ¹⁹⁵Pt, δ [p.p.m., to high frequency of Ξ (¹⁹⁵Pt) = 21.4 MHz] 1651 [J (WPt) 177 Hz].

Crystal-structure Determinations.—Complex (1), [Pt{W(CC₆H₄Me-4)(CO)₂(η -C₅H₅)₂}]. Crystals of (1) grow as red-purple elongated octahedra, truncated axially, from solution in light petroleum. Diffracted intensities were

collected at 200 K from a crystal of dimensions $0.28 \times 0.42 \times 0.28$ mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.^{28,29} Of the total 6 189 reflections measured for $2.9 \leq 2\theta \leq 55^\circ$, 4 369 which satisfied the criterion $F > 3\sigma(F)$ after correction for Lorentz, polarisation, and X-ray absorption effects were used in the solution and refinement of the structure. Three reflections ($\bar{5} 0 \bar{2}$, $4 0 4$, and $1 1 \bar{1}$) were remeasured every 50 reflections; no significant crystal decay was apparent.

Crystal data for (1). $C_{30}H_{24}O_4PtW_2$, $M = 1 010.6$, Monoclinic, $a = 12.187(6)$, $b = 13.404(7)$, $c = 16.938(9)$ Å, $\beta = 96.42(4)^\circ$, $D_m = 2.36$ g cm⁻³, $Z = 4$, $D_c = 2.39$ g cm⁻³, $U = 2 749$ Å³, $F(000) = 1 847$, space group $P2_1/c$ (no. 14), Mo- K_α X-radiation (graphite monochromator), $\lambda = 0.710 69$ Å, $\mu(\text{Mo-}K_\alpha) = 137.0$ cm⁻¹.

Structure solution and refinement for (1). The structure was solved by heavy-atom methods and the hydrogen atoms, which were not located with any certainty in the electron-density maps, were incorporated at calculated positions (C-H = 1.08 Å) with isotropic group thermal parameters for methyl H atoms $[0.10(5)$ Å²] and for cyclopentadienyl and aromatic H atoms $[0.04(1)$ Å²]. All other atoms were allowed anisotropic thermal motion. Refinement was by blocked-matrix least squares, with an optimised weighting scheme of the form: $w = 0.753 [\sigma^2(F) + 0.001 5|F|^2]^{-1}$, where $\sigma(F)$ is the estimated error in $|F_{\text{obs}}|$ based on counting statistics only. Convergence was reached at $R 0.047$ ($R' 0.048$), and the final electron-density difference synthesis showed no peaks of any significance except in the vicinity of the metal atoms, where residues of ca. $2 e \text{ \AA}^{-3}$ were observed. Atomic scattering factors were those of ref. 30 for hydrogen and ref. 31 for all other atoms. All computations were carried out on the South Western Universities' Computer Network with the 'SHELX' system of programs.³²

Complex (2), $[Ni\{W(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\}_2]$. Crystals of (2) grow as dark red prisms from dichloromethane-pentane solution at -20°C . Experimental details are as for (1) with the following exceptions: temperature, 295 K; crystal size, $0.20 \times 0.07 \times 0.05$ mm; Syntex P3 diffractometer; $2.9 \leq 2\theta \leq 65^\circ$, 8 586 reflections of which 5 246 had $I > 3\sigma(I)$. No absorption correction was made; an attempt to do so resulted in unstable refinement and meaningless physical parameters, presumably because of insufficient accuracy in measurement of the crystal shape.

Crystal Data for (2). $C_{30}H_{24}NiO_4W_2$, $M = 874.9$, Monoclinic, $a = 7.980(2)$, $b = 22.080(6)$, $c = 16.025(3)$ Å, $\beta = 103.45(2)^\circ$, D_m not measured, $Z = 4$, $D_c = 2.12$ g cm⁻³, $U = 2 747$ Å³, $F(000) = 1 648$, space group $P2_1/n$ (no. 14), $\mu(\text{Mo-}K_\alpha) = 87.4$ cm⁻¹.

Structure solution and refinement for (2). The structure was solved by heavy-atom methods using the 'SHELXTL' system³³ of programs on an 'Eclipse' (Data General) minicomputer, and was refined using a blocked-cascade least-squares method. One of the cyclopentadienyl rings showed in-plane disorder; atom co-ordinates C(31)—(35) and C(41)—(45) indicate the two sets of positions (see Table 4) and occur in a population ratio of 7 : 3, respectively. Hydrogen atoms for the tolyl rings were first incorporated at calculated positions and then allowed to refine with a common isotropic thermal parameter, while those for the methyl and cyclopentadienyl groups were restrained to 'ride' on the corresponding carbon atom and were given

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

isotropic thermal parameters equal to $1.2 U_{\text{iso}}$, for the carbon atom. The carbon atoms of the disordered cyclopentadienyl rings were constrained to refine as regular pentagons. Weights were of the form $w = [\sigma^2(F) + 0.001 3|F_o|^2]^{-1}$, and convergence was obtained at $R 0.053$ ($R' 0.063$). Scattering factors were from ref. 30 for hydrogen, ref. 34 for carbon and oxygen, and ref. 31 for nickel and tungsten. In both structures, corrections for anomalous dispersion of the metal atoms were made.^{31,35} Observed and calculated structure factors, positional and thermal parameters for the hydrogen atoms, and all the thermal parameters are listed in Supplementary Publication No. SUP 22964 (57 pp.).*

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